Tetrahedron Letters No. 18, pp 1755 - 1757, 1972. Pergamon Press. Printed in Great Britain.

ELECTROPHILIC AROMATIC SUBSTITUTION VII.[1] THE EFFECT OF NITROSATION ON THE ORTHO: PARA-RATIO IN NITRATION OF BIPHENYL

By R. Taylor

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, England

(Received in UK 8 March 1972; accepted for publication 22 March 1972)

Coombes and Russell[2] have recently reported that the nitration of biphenyl in very dilute solution (4×10^{-5} mol 1^{-1}) in an aqueous nitric acid-sulphuric acid medium (57-68 wt-% sulphuric acid containing 2×10^{-3} - 5×10^{-2} mole 1^{-1} nitric acid and 3×10^{-2} mol 1^{-1} urea) at 25° gives rise to very high *ortho*:*para*-ratios of 3·3 and 3·7 (both ±0·6). As a consequence, they have suggested that the *low*-ratios (*ca*. 0·6 - 1·4) previously obtained [3-5] in nitric acid-sulphuric acid mixtures may be abnormal and arise from nitration *via* nitrosation. They also suggest that the high ratios obtained in nitric acid-acetic anhydride (*ca*. 2·0 - 2·75) and dinitrogen pentoxide in acetonitrile (*ca*. 2·6 - 2·8) are normal for biphenyl nitration and arise from reaction with the nitronium ion, no special mechanism for enhanced *ortho* nitration being required to explain the results in these media (*cf*. refs. 3). We therefore report further results from nitration in nitric acid-sulphuric acid mixtures.

Firstly we have nitrated biphenyl under the conditions described as homogeneous by Coombes and Russell, and we confirm both the high *ortho*:*para*-ratio, and the absence of significant dinitration. However we were unable to prepare solutions of biphenyl in sulphuric acid in the concentrations they describe, and even in 68% acid (the best solvent of the range) the biphenyl appeared largely undissolved even after stirring during 24 hr. at 25°. (Biphenyl appears to dissolve more readily in the presence of the nitric acid because the nitrobiphenyl reaction products are more soluble in sulphuric acid.) Runs were therefore carried out by depositing the stated amount of biphenyl as a film on the walls of the reaction flask, into which was added the nitrating mixture, the whole being then stirred for the required reaction time. Even under these conditions, the extent of nitration showed some dependence upon the stirring rate (increasing with increase in the latter), so that we have some doubts that these results relate to truly homogeneous nitration.

Secondly for nitration with the more concentrated nitric acid-sulphuric acid solutions (which are much better solvents) and under the conditions formerly used by us, we now find the ortho:para-ratio to be very dependent upon the source of the nitric acid. Previously[3], and in the present work, nitrations were carried out with a mixture of 60 wt-% nitric acid in 98% sulphuric acid, and solutions of biphenyl in nitrobenzene at 50°, dinitration being unimportant under these conditions[3]. In our earlier work this dilute nitric acid was prepared from fuming nitric acid (for consistency with other workers[4]), and the resultant ortho:para-ratios were ca. 0·7 - 0·8; ratios in this range were reobtained in the present studies using these conditions (the value is reduced slightly in the presence of more sulphuric acid). If however runs were performed with dilute nitric acid prepared from 70 wt.-% nitric acid (d, 1·42) then higher ratios of ca. 1·4 were obtained, (and the nitration rate was slower) and it seems likely therefore that nitrosation is affecting the ratio.

To confirm this we firstly added urea to the mixture prepared from fuming nitric acid and found the ratio to increase to a maximum of 1·4 (and the nitration rate decreased). However it should be noted that the value could not be exceeded even in solutions saturated with urea. Furthermore, the addition of sodium nitrite to the nitrating mixture prepared from 70% nitric acid caused a reduction in the ortho:para-ratio to the value of 0·6 (and an increase in reaction rate), whereas addition of urea produced no change in the ratio of 1·4.

It is clear then that nitrosation is an important factor in affecting the ortho:para-ratio for nitration of biphenyl in nitric acid-sulphuric acid, causing a decrease in the value, and an increase in the reaction rate. This results parallels that found recently[6] for nitration of anisole in sulphuric acid. The ortho:para-ratio of 1·5 was decreased to 0·065 in the presence of sodium nitrite showing that under the latter conditions nitration proceeds *via* nitrosation which preferentially occurs at the *para* position. Presumably the lower ratio from nitrosation reflects the lower reactivity of the nitrosonium ion, and a comparable change in the ratio from 2·0 to 0·38 occurs in hydrogen exchange of biphenyl as the reactivity of the exchanging acid is decreased[7].

With regard to the present results the following points are stressed. Firstly, the maximum ratios obtainable in the concentrated acid solutions (even when saturated with urea) are much less than those obtained with nitric acid-acetic anhydride, and dinitrogen pentoxide in acetonitrile. Secondly, the reacting species in the concentrated acid media is unquestionably nitronium ion, and here the rate of reaction is likely to be very much less than the rate of encounter, in contrast to the situation in the dilute acid media. Thirdly, the nitrosation-free *ortho*:*para*-ratio in the concentrated acid media is both theoretically reasonable and consistent with all other electrophilic substitutions of biphenyl[7]; this contrasts with the results obtained in the dilute acid media, and in acetic anhydride and acetonitrile.

We therefore conclude that the results of Coombes and Russell do not reflect normal nitration of biphenyl by nitronium ion, being most probably vitiated as they propose by problems of encounter control. It also follows that a special mechanism for *ortho*-substitution for nitration in acetonitrile and acetic anhydride, such as that which we previously proposed[2], is still required at this time.

REFERENCES

1. Part VI. F.P. Bailey and R. Taylor, *J.Chem.Soc.(B)*, 1971, 1446.
2. R.G. Coombes and L.W. Russell, *J.Chem.Soc.(B)*, 1971, 2443.
3. R. Taylor, *J.Chem.Soc.(B)*, 1966, 727; *Tetrahedron Letters*, 1966, 6093.
4. R.L. Jenkins, R. McCullough, and C.F. Booth, *Ind. Eng. Chem.*, 1930, *22*, 31.
5. C.J. Billing and R.O.C. Norman, *J.Chem.Soc.*, 1961, 3885.
6. J.G. Hoggett, R.B. Moodie, and K. Schofield, *Chem.Comm.*, 1969, 605.
7. R.O.C. Norman and R. Taylor, *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, Amsterdam, 1965.